Journal of Thermal Analysis Vol. 33 (1988) 1003–1012

STUDY OF THE BINARY $CaCO_3$–SiO_2 SYSTEM BY QUANTATITATIVE DTA

K. Sinkó, L. Pöppl, M. Gábor and *B. Migály*+

INSTITUTE OF INORGANIC AND ANALYTICAL CHEMISTRY,
L. EÖTVÖS UNIVERSITY, BUDAPEST
+CENTRAL RESEARCH AND DESIGN INSTITUTE FOR THE SILICATE
INDUSTRY, BUDAPEST, HUNGARY

Solid-state reactions in the $CaCO_3$–SiO_2 system with different mass ratios ($CaCO_3 : SiO_2$ = from 1 : 0.2 to 1 : 10) were studied by means of thermogravimetry, quantitative DTA and high-temperature X-ray diffraction up to 1500 °C.

It was found that not $CaCO_3$, but CaO reacted with SiO_2. The rate of decarboxylation increased and the temperature of formation of silicate phases decreased significantly with increasing silica content. Only mono- and dicalcium silicates could be detected as solid-state reaction products. Above 1400 °C, an intensive melting process took place; the amount of silica had no clear effect on its temperature range.

Quantitative DTA and X-ray diffraction data proved that, below 1000 °C, not only the decarboxylation process, but also silicate formation must be taken into consideration.

There is a contradiction in the literature as to whether SiO_2 reacts with $CaCO_3$ as such or after its decomposition to CaO. Most of the data show that silicate formation takes place only after decarboxylation [9–3]. Below 1000°, only CaO formation need be taken into consideration. According to Kröger [4], there is already an equilibrium between $CaSiO_3$, Ca_2SiO_4 and $3CaO \cdot 2SiO_2$ below the dissociation temperature of limestone (770–870°).

There are only a few data describing processes above 1000°. In the binary system, Kautz et al. [5] found only CaO as a new phase up to 1100°. Tamman and Oelsen [6] detected wollastonite formation at 1010°, while Wilburn and Thomasson [3, 7] found meta- and orthosilicates, depending upon the composition. If SiO_2 was in excess, metasilicate could be identified as the main product at 1200°. If $CaCO_3$ was in excess, than the main product was the orthosilicate, which formed above 1400°.

The aim of this research was to study the $CaCO_3$–SiO_2 system by means of simultaneous TG–DTA up to 1500°, and by high-temperature X-ray diffraction measurements for the identification of new phases formed during the transformations.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Thermoanalytical investigations were carried out with a Mettler Thermoanalyser in the temperature range 25–1500°, in flowing synthetic air. The heating rate was 6 deg min^{-1}, and the crucible material was sintered Al_2O_3.

The high-temperature X-ray diffraction measurements were performed with a JEOL JDX–85 instrument (accelerating voltage 40 kV, 40 mA) in a platinum-rhodium sample holder. The heating rate here too was 6 deg min^{-1}.

The samples were $CaCO_3$ and SiO_2 of analytical purity. The particle size was less than 53 and 71 μm, respectively.

Results and discussion

In the first part of the investigations, the aim was to study the chemical reactions between SiO_2 and $CaCO_3$ in the temperature range 25–1500°, and to learn how the $SiO_2/CaCO_3$ ratio influences this reaction. The results of thermoanalytical investigations are summarized in Table 1. Table 2 gives the X-ray diffraction data on these samples at 25–1500°; the temperature ranges where a new phase appeared or an existing one disappeared are specially mentioned. The X-ray data on $SiO_2/CaCO_3$ mixtures with mass ratios of 0.2 and 10 are missing, since they were not identifiable.

Table 1 shows that the firt endothermic DTA peak, between 560 and 575°, relates to the α-β polymorphic transformation of SiO_2, and that the $SiO_2/CaCO_3$ ratio has no effect on this transformation. X-ray diffraction measurements indicate this transformation between 500 and 550°.

The DTA peak in the temperature range 640–870° relates to the decarboxylation of $CaCO_3$ (calcite), which is accompanied by a DTG peak in this temperature range. The starting of decarboxylation (see the initial temperatures of the DTA and DTG peaks: 580–600°) are not influenced by the quantitative composition of the binary system. However, increase of the amount of SiO_2 significantly accelerates the decarboxylation process, with decreases in the maximum and final temperatures of the DTA and DTG peaks. Thus, the temperature range of decomposition is reduced by 70–80 deg.

As concerns the X-ray data (Table 2) relating to the complete reaction of calcite and the formation of silicate, these proved that SiO_2 reacts not with $CaCO_3$, but with CaO. New phases were detected only after the complete decarboxylation, but already below 1000°, in contrast with observations published in the literature.

By means of X-ray diffraction, only dicalcium and monocalcium silicate could be identified as new phases, independently of the ratio of SiO_2 to $CaCO_3$ in the sample.

Table 1 Summary of thermoanalytical investigations. Peak temperature in function of $SiO_2/CaCO_3$ ratio

$SiO_2/CaCO_3$ mass-ratio	Temperature-range of DTA-peaks									Temperature-range of DTG-peaks		
	initial, °C	max., °C	final, °C	initial, °C	max., °C	final, °C	initial, °C	max., °C	final, °C	initial, °C	max., °C	final, °C
0.2	—	—	—	648	850	872	1412	1419*– 1445*	1451	629	851	872
0.6	560	566	572	638	841	860	1421	1437	1447	604	828	869
1	560	566	575	656	827	851	1408	1435	1459	596	820	860
2	559	565	572	641	813	831	1409	1434	1441	594	808	852
3	557	565	572	644	800	809	1407	1434	1441	601	793	821
5	557	566	571	644	782	794	1411	1434	1438	603	773	804
10	561	568	576	650	781	791	1409	1431	1440	596	771	795

* exotherm

Table 2 Temperature-range of phase changes by X-ray diffraction method

$SiO_2/CaCO_3$ mass-ratio	Temperature-range of phase changes °C										
	disapp. of $CaCO_3$ (calcite)	CaO		$Ca_3Si_3O_9$ (wollastonite)			disapp. of cyclowollastonit	Ca_2SiO_4 (orthosilicate)			SiO_2 (quartz) disapp.
		app.	disapp.	app.	transf.*	disapp.		app.	transf.**	disapp.	
0.6	630–650	590–600	1340– 70	950–960	—	1420– 40	—	920–950	1420–30	>1500	1400– 20
1	630–650	570–590	1380–1400	900–950	1320– 30	1330– 50	1380–1400	850–870	—	1380–1400	1380–1400
2	630–650	580–600	1360– 80	820–850	1290–1300	1360–180	1460– 90	850–870	—	1420– 50	>1500
3	620–650	550–580	1340– 60	790–800	1300– 20	1370– 90	1340– 50	800–820	—	1400– 20	>1500
5	600–650	550–560	1120–1150	650–750	1250–1300	1260–1300	1350– 70	750–800	—	1380–1400	>1500

* polymorphic transformation of wollastonite-cyclowollastonite ($CaSiO_3$)
** polymorphic transformation of orthosilicate (α)
disapp. = disappearance
app. = appearance
transf. = transformation

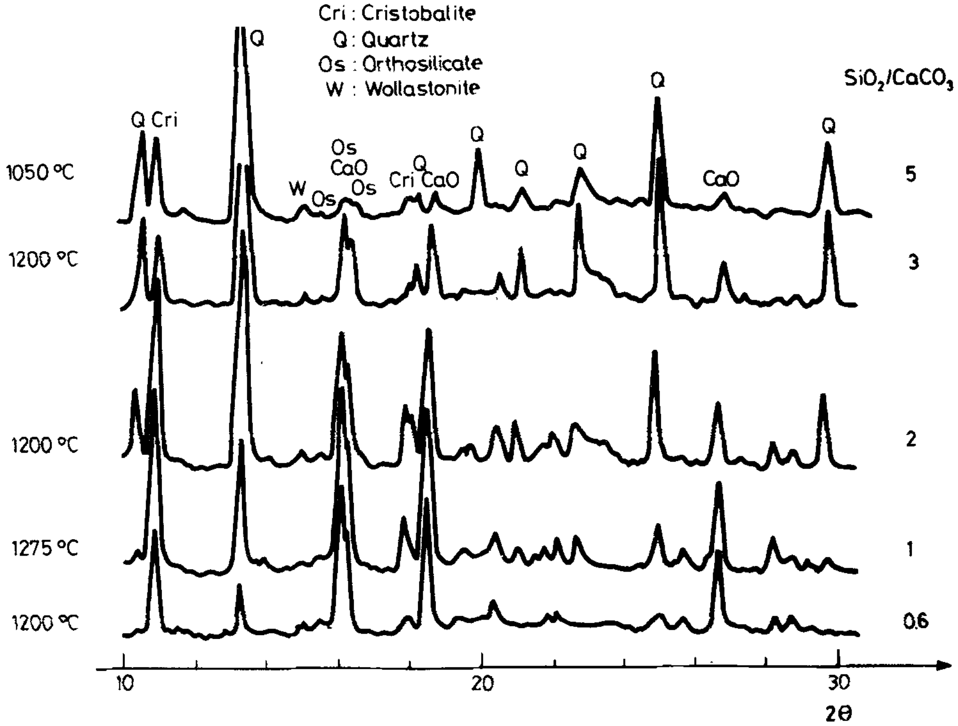

Fig. 1 High temperature X-ray diffraction patterns obtained for $SiO_2/CaCO_3$ systems with different mass ratio

Dicalcium silicate was present in a more considerable quantity at every composition (Table 1).

Figure 1 shows high-temperature X-ray diffraction-diagrams of samples with different compositions at the temperatures where the intensities and quantities of CaO and dicalcium silicate are approximately equal.

Detection of monocalcium silicate became uncertain at 900–1200°, its degree of crystallization is poor when it is present in small quantity.

The reason for the predominance of orthosilicate in the diffractograms (independently of the mixture composition) is that there is not enough time for equilibration at the heating rate of 6 deg min^{-1}. (This holds for industrial conditions too!) Kinetic control is more effective. Yung and Fateeva [8] found that, in the event of quick heating, the most probable process is the formation of orthosilicates, since the reaction rate of orthosilicate is the lowest of all.

The X-ray diffraction data (Table 2) and X-ray diagrams (Fig. 1) show that under these conditions the complete reaction of CaO and SiO_2 is achieved very slowly.

CaO disappears from the system only far above 1300°, and quartz disappears at about 1400° (if it is not in excess), forming a molten phase.

This low reaction rate and the non-quantitative reaction is the reason why silicate formation is not indicated by a DTA peak.

The formation of silicate is promoted considerably by increase of the amount of SiO_2 in the mixture: the temperature range of appearance of calcium silicates (shown by X-ray diffraction measurements) then decreases by 150–200 deg.

In most cases, wollastonite is transformed to cyclowollastonite at about 1300° (Table 2). This is proven by the fact that, as cyclowollastonite appears in the system, wollastonite disappears from it at about 1300–1350°. The $SiO_2/CaCO_3$ ratio of the mixture has no effect on the temperature of this transformation. According to Wilburn and Thomasson [3], the endothermic peak near 1270–1280° relates to this polymorphic transformation of wollastonite. However, according to other thermal data on wollastonite, this transformation takes place at about 1125–1190°.

Our thermoanalytical investigations show an endothermic effect above 1400°, with a peak maximum at 1435°, independently of the quantitative composition of the sample. Wilburn et al. [3, 7] found that the endothermic peak between 1410–1420° relates to the formation of orthosilicate, and the endothermic peak at about 1430° to the polymorphic transformation of orthosilicate.

Our X-ray measurement data are inconsistent with Wilburn's observations. Orthosilicate is already detectable below 1000°. The polymorphic transformation of dicalcium silicate could be observed only in the sample with 1 : 1 mole ratio (0.6 : 1 mass ratio), and only at low intensity. This transformation could not cause such a considerable and sharp endothermic change in the DTA curve.

High-temperature X-ray measurements show the disappearance of different crystalline phases: calcium silicates, CaO, quartz if SiO_2 is not in excess, and cristobalite. From all these results, the conclusion can be drawn that sharp and intensive melting occurs.

This conclusion was supported by the findings on samples heated above 1400° and then cooled down. Samples heated up to 1400° were still in the powder state, and there was no molten phase. Samples heated up to 1420–30° suddenly melted or (depending on the composition) just started to melt. The only exceptions were the samples with extreme (5/1 and 1/5) mass ratios. They were still in the powder state at 1460° or sintered to a minimal degree.

X-ray diffractograms of samples heat-treated between 1400 and 1460° and then cooled down to room temperature (although they are quite different from the high-temperature X-ray data in Fig. 2) did not prove either the formation of new phases or the polymorphic transformation. Samples heat-treated between 1400 and 1430° contained cyclowollastonite or γ-dicalcium silicate as main component at room

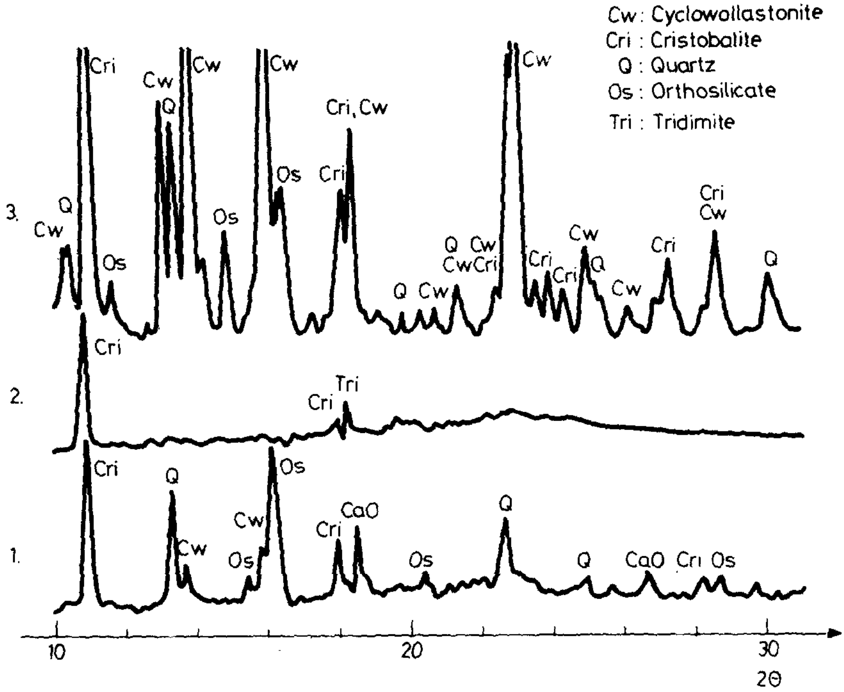

Fig. 2 X-ray diffraction patterns obtained for $SiO_2/CaCO_3$ system with 1 : 1 mass ratio. 1. at 1375 °C, 2. at 1400 °C, 3. as 2. but cooled down to room temperature

temperature, together with (depending on the composition) various amounts of CaO, quartz or cristobalite.

In these samples, the nature of the calcium silicate already depends upon the composition. At a mole ratio of 1 : 1 or in a SiO_2 excess, cyclowollastonite was found as main component, with only a small amount of wollastonite. If $CaCO_3$ was in excess, γ-dicalcium silicate was the main component. In this case, the more effective rules were the thermodynamic, and not the kinetic ones.

If SiO_2 was not in excess, cristobalite and dicalcium silicate disappeared from the mixture heat-treated in the temperature range 1430–1460°, but if SiO_2 was in excess, only a change in intensity could be observed.

Heat treatment was performed in a sintered Al_2O_3 crucible, similarly as in thermodynamic investigations. The X-ray measurements detected small amounts of gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$, which proved the reaction between the samples and the crucible. According to the X-ray measurements, gehlenite could be formed only after the formation of a molten phase.

Since there is a difference between the X-ray diagrams of samples heated up to high

Table 3 Quantitative DTA-data of $CaCO_3$–SiO_2 system

Sample mass ratio	α-β transformation of quartz			Decarbonization $CaCO_3$			DTA changes above 1400 °C		Total ΔH, J/g
	DTA-peak temp., °C	ΔH, J/g mixture	ΔH, J/g quartz	DTA-peak temp., °C	ΔH, J/g mixture	ΔH, J/g $CaCO_3$	DTA-peak °C	ΔH, J/g mixture	
$CaCO_3$	—	—	—	821	—	1776	—	—	1776
$aeSiO_2/CaCO_3 = 0.2$	—	—	—	850	1575	1890	1419 ex* 1445 ex*	$\left.\begin{matrix}36\\65\end{matrix}\right\}101$	1474
$SiO_2/CaCO_3 = 0.6$	566	3.7	9.9	841	1291	2066	1437	92.6	1387
$SiO_2/CaCO_3 = 1$	566	6.7	13.5	827	1062	2125	1435	129.5	1198
$SiO_2/CaCO_3 = 2$	565	7.4	11.1	813	679	2038	1434	102.0	788
$SiO_2/CaCO_3 = 3$	565	11.0	14.7	800	481	1924	1434	95.7	588
$SiO_2/CaCO_3 = 5$	566	8.6	10.4	782	275	1650	1434	65.7	349
$SiO_2/CaCO_3 = 10$	568	11.7	12.9	781	156.5	1721	1431	59.0	227

* exotherm. DTA-peak

temperature and then cooled down to room temperature and the high-temperature X-ray diagrams (Fig. 2), it is important to follow the high-temperature processes at the temperatures of transformations. Conclusions drawn from the cooled samples can be accepted only with certain restrictions.

Table 3 summarizes the data from quantitative DTA measurements. Data from parallel measurements differ from the average value by only 5–10%.

The decarboxylation heat of $CaCO_3$ of analytical purity is 1776 ± 170 J g^{-1}, in accordance with published values (e.g. 1778 J g^{-1} [11, 12] and 1611 J g^{-1} at 827° [13].

Energy values relating to the DTA peaks near 565° could be identified as due to the α-β transformation of SiO_2, value of which is 12.1 J g^{-1} [10]. Our measurements were scattered around this value, but the average energy was also 12.1 J g^{-1}.

The heat relating to the endothermic DTA peak between 640 and 870° is naturally decreased on increase of the quantity of SiO_2. If the data are referred to the $CaCO_3$ content of the mixture (Table 3, column 7) one finds that $\Delta H'$ passes through a maximum at a 1 : 1 mole ratio. At higher or lower ratios, $\Delta H'$ approaches the decarboxylation enthalpy of $CaCO_3$. From these data, it can be inferred that not only the decarboxylation, but also other transformations, should be taken into consideration in the above temperature range. If one of the components is in excess, the possibility of formation of calcium silicates decreases. Comparison of the peak intensities of the X-ray diagrams also confirms the thermoanalytical observation that the formation of silicates is the greatest at a mole ratio and mass ratio of 1 : 1.

The heat associated with the endothermic peak above 1400° changes in parallel with that of the DTA peak between 640 and 870°, referred to the $CaCO_3$ content. Thus, there is a strong connection with the quantity of silicates formed in this process, with their melting in this temperature range, and with the quantity and melting of CaO.

The total ΔH values are decreased considerably by decrease of the $CaCO_3$ content of the mixture, since the most significant change of heat content in the thermoanalytical investigations is caused by decarboxylation.

References

1 A. Niggli, Z. Anorg. Chem., 98 (1916) 241.
2 S. Turner, J. Soc. Glass Technol., 16 (1932) 94.
3 F. W. Wilburn, and C, Thomasson, Phys. Chem. Glass, 2 (1961) 126.
4 C. Kröger and G. Ziegler, Glastechnische Ber., 26 (1953) 346.
5 K. Kautz and G. Stromburg, Glastechn. Ber., 42 (1969) 309.
6 Tamman and Oelsen, Z. Anorg. All. Chem., 193 (1930) 245.
7 R. Warburton and F. W. Wilburn, Phys. Chem. Glass, 4 (1963) 91.

8 V. N. Yung and N. S. Fateeva, Tsement Moscow, 20 (1954) 11.
9 Gmelin, Handbuch Verlag Chemie, Weinheim 1961, Band 28/3.
10 I. Barin and O. Knacke, Thermochemical properties of inorganic substances, Springer-Verlag, 1973 182/689.
11 H. Elsner von Gronow, Zement, 25 (1936) 421.
12 W. Blitz, G. Rohlfs and H. Vogel, Z. Anorg. Chem., 220 (1934) 114.
13 J. Johnston, J. Am. Soc., 32 (1910) 938.

Zusammenfassung — Die Festkörperreaktionen im System $CaCO_3$–SiO_2 in Mischungen mit Masseverhältnissen 1 : 0,2 bis 1 : 10 wurden durch TG, quantitative DTA und Hochtemperatur-Röntgenbeugung untersucht. Es wurde gefunden, dass $CaCO_3$ als CaO mit SiO_2 reagiert. Mit zunehmendem Gehalt der Mischungen an SiO_2 nimmt die Geschwindigkeit der CO_2-Abspaltung zu, die Temperatur der Silicatbildung wird deutlich erniedrigt. Als Produkte der Festkörperreaktion wurden nur Monocalcium- und Dicalciumsilicat nachgewiesen. Oberhalb 1400 °C erfolgt ein Schmelzprozess, dessen Temperatur vom SiO_2-Gehalt in komplizierter Weise beeinflusst wird. Quantitative DTA und Röntgenbeugung zeigten, dass bereits unterhalb 1000 °C nicht nur die CO_2-Abspaltung sondern auch Silicatbildungsreaktionen in Betracht zu ziehen sind.

Резюме — Методом термогравиметрии, количественного ДТА и высокотемпературного фазового анализа изучены в области температур 25–1500° твердотельные реакции в системе $CaCO_3$:SiO_2 с весовым соотношением компонент от 1:0,2 до 1:10. Установлено, что в реакцию с двуокисью кремния вступает не карбонат кальция, а образующаяся из него окись кальция. Скорость реакции декарбонилирования увеличивается, а температура образования силикатных фаз значительно уменьшается с увеличением содержания двуокиси кремния. В продуктах твердотельных реакций были найдены только моно- и дикальций силикаты. Выше 1400° имеет место интенсивный процесс плавления, однако влияние на его температурный интервал двуокиси кремния не совсем ясно. Количественный ДТА и рентгенофазовый анализ показали, что ниже 1000° следует учитывать не только процесс декарбонилирования, но и образование силикатов.